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NASA Case No. LEW-15,714-1

PRINT FIG. 1

NOTICE

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Serial No.: 08/221,128

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(NASA-Case-LEW-15714-1) CERAMIC  
FIBER-REINFORCED MONOCLINIC CELSIAN  
PHASE GLASS-CERAMIC MATRIX  
COMPOSITE MATERIAL Patent  
Application (NASA. Lewis Research  
Center) 14 p

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Ceramic Fiber-Reinforced Monoclinic Celsian  
Phase Glass-Ceramic Matrix Composite Material

Origin of the Invention

The invention described herein was made by employees of the U.S. Government and may be manufactured and used by or for the Government for governmental purposes without the payment of any royalties thereon or therefor.

Statement of Copendency

This application is a continuation-in-part of copending application serial No. 07/986,399 which was filed December 7, 1992.

Technical Field

This invention is directed to an improved composite material for use at temperatures up to 1300° C as well as a method of making this material. The invention is particularly directed to a material for use in radome applications at high temperatures.

New radome materials are needed for future advanced tactical missiles. Materials having low and thermally stable dielectric constants and loss tangents, low thermal expansion coefficients, and high thermal shock and rain erosion resistances are required for use at temperature as high as 1300° C. Fused silica has good dielectric and thermal properties for radomes, but this material shows low strength, low fracture toughness, and poor rain erosion resistance.

Monoclinic celsian phase  $\text{BaO-Al}_2\text{O}_3\text{-}2\text{SiO}_2$  (BAS) has low thermal expansion, low dielectric constant and loss, and phase stability up to 1590° C. However, this material suffers from poor mechanical strength and low fracture toughness.

It is, therefore, an object of the present invention to provide a new composite material having superior mechanical properties for use in radomes.

Another object of the invention is to provide a strong and tough composite material having a low dielectric constant, ( $\epsilon$ ), low dielectric loss, and which shows small changes in dielectric

constant over a large temperature range.

Still another object of the invention is to provide a method of fabricating an improved fiber-reinforced celsian matrix composite material having superior dielectric properties along with good mechanical strength and fracture toughness compared with the existing dielectric materials, particularly at high use temperatures.

#### Background Art

U.S. patent No. 4,857,485 to Brennan et al is directed to fiber reinforced articles of lithium, alumino-silicate glass ceramic which may include barium oxide. U.S. patent No. 4,869,858 to Funayama et al discloses a process for producing polysiloxazane fibers which can be used as precursors of silicon oxynitride fibers which are used as reinforcement in composite materials.

U.S. patent No. 5,024,979 to Debaig-Valade et al is concerned with a method of forming a fibrous structure composite ceramic which may include silazanes as organometallic precursors to the ceramic materials. U.S. patent No. 5,055,431 to Blum et al describes polysilazanes which can be combined with other ceramic powders to produce composite articles.

U.S. patent No. 5,077,243 to Nakano et al describes a method of forming a fibrous structure composite ceramic. The material may include silazanes as organometallic precursors of the ceramic materials.

#### Disclosure of the Invention

The aforementioned objects of the invention are achieved by the invention which relates to hydridopolysilazane-derived ceramic fiber reinforced monoclinic celsian phase glass-ceramic matrix composites. The fibers improve the mechanical strength and fracture toughness. These fibers further provide superior dielectric properties.

The composite uses thin ceramic fibers having low dielectric

constants with good thermal stability and oxidation resistance. The fibers are precoated with thin ceramic coatings. This provides a weak fiber-matrix interface for composite toughness.

5       The process includes the steps of (1) precoating the ceramic fibers with ceramic films having low dielectric constants, good thermal stability, and oxidation resistance, (2) passing the coated ceramic fibers through a wet ground BAS bed, (3) spooling the fibers about a take up drum, (4) cutting the spooled  
10       material, stacking the cut material in a desired orientation, and warm pressing to produce a green laminate, (5) heating the green laminate to burn out organics, and (6) hot pressing the resulting stack for consolidation.

#### Description of the Drawings

15       The objects, advantages and novel features of the invention will be more fully apparent from the following detailed description when read in conjunction with the accompanying drawings:

20       FIG. 1 is an optical photograph showing part of the 4.5"x2" composite panel of BAS glass-ceramic matrix reinforced with fiber having a double coating of BN/Si<sub>3</sub>N<sub>4</sub> and hot pressed at 1400° C for 2 hrs. at 3.5 KSI;

25       FIG. 2 is a scanning electron micrograph of a polished cross-section of a double coated fiber-reinforced BAS glass-ceramic matrix composite hot pressed at 1400° C for 2 hrs. at 3.5 KSI showing uniform fiber distribution; and

      Figs. 3 and 4 are scanning electron micrographs of fracture surfaces of double coated fiber-reinforced BAS matrix composites showing fiber pull out indicating toughened composite behavior.

#### Best Mode for Carrying Out the Invention

30       According to the present invention the new composite material has superior mechanical properties and is well adapted to use in radomes. This material comprises BaO-Al<sub>2</sub>O<sub>3</sub>-2 SiO<sub>2</sub> (BAS)

glass-ceramic matrix having monoclinic celsian as the only crystalline phase which is reinforced with continuous hydridopolysilazane-derived ceramic fibers. These fibers are prepared from hydridopolysilazane polymer by a pyrolytic process and marketed by Dow Corning as HPZ fibers. The HPZ fiber has an oval cross-section and is amorphous with a typical elemental composition of 57% Si, 28% N, 10% C and 4% oxygen.

The fiber-reinforced BAS (celsian) glass-ceramic matrix composite material is fabricated in accordance with the present invention by using a slurry process. An aqueous slurry of BAS glass powder having an average particle size of about 2.5  $\mu\text{m}$  along with a fugitive organic binder, plasticizer, defloculant, surfactant, and about 10 to about 20 weight percent of fine monoclinic celsian seeds is first ball-milled.

The hydridopolysilazane-derived ceramic fibers are coated with glass matrix by passing them through this slurry. The coated fibers are then wound onto a take up drum where they are allowed to dry. The resulting prepreg sheets are cut into mats having desired geometries, stacked to obtain a predetermined fiber orientation, and warm pressed to produce a "green" composite.

The "green" composite is further consolidated by hot pressing under vacuum using appropriate temperatures, pressures and times. Temperatures in the 1200° C to 1400° C range have been satisfactory.

The organic materials are burned out in situ in the hot press at a lower temperature in air. A coating of an appropriate material, such as boron nitride or double coatings such as BN/Si<sub>3</sub>N<sub>4</sub> or BN/SiC, may be required on the hydridopolysilazane-derived ceramic fiber surface to protect the fibers from bonding with the matrix during hot pressing.

Description of Alternate Embodiment of the Invention

Celsian formation in the glass-ceramic matrix can also be facilitated by substituting 5 to 10 weight percent of BaO by SrO in the glass batch during melting prior to forming the glass powders as set forth in copending application serial No.

07/872,262 which was filed April 16, 1992 and is now abandoned.

This is described in U.S. patent No. 5,214,004. This BSAS matrix is used in the same manner as the previously described BAS matrix in improved composites. These composites consist of  $x\text{BaO} \cdot (1-x)\text{SrO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$  (BSAS) [where  $x$  varies from 0 to 1] glass-ceramic matrix, having monoclinic celsian phase, reinforced with continuous silicon nitride-based ceramic fibers such as

hydridopolysilazane derived (HPZ) fibers previously described.

The thermal expansion coefficient of the HPZ fibers is  $3 \times 10^{-6}/^\circ\text{C}$ , which gives a good expansion compatibility with the BSAS celsian glass-ceramic matrix having a thermal expansion coefficient of  $2.5 \times 10^{-6}/^\circ\text{C}$ .

An important feature of this embodiment is that the fibers are precoated with thin ceramic materials ( $1\mu\text{m}$ ). The ceramic coating materials have a low dielectric constant, are thermally stable and oxidation resistant, and provide weak fiber-matrix interface for composite toughness.

The HPZ fiber-reinforced BSAS glass-ceramic matrix composites are fabricated in two-dimensional (2D) laminate form using a slurry method previously described. More particularly, an aqueous slurry is ball milled using BSAS glass powder having an average particle size of about  $2.5\mu\text{m}$  along with a fugitive organic binder, plasticizer, deflocculant, surfactant, and 10 to 20 weight % of fine monoclinic celsian seeds for matrix compositions with  $x$  greater than 0.95.

After precoating as set forth above for toughness control, the continuous ceramic-fibers are again coated with the glass

matrix by passing through the slurry, wound on a take-up drum, and allowed to dry. The prepeg sheets are cut into desired geometry, stacked to obtain desired fiber orientation, and warm  
5 pressed resulting in a "green" laminate composite.

The "green" composite can be further consolidated by hot pressing under vacuum using appropriate temperature (1200 to 1400°C), pressure, and time. The organics are burned out in situ in the hot press at a lower temperature.

10 The interface coating composed of an appropriate material, such as BN or a double coating of BN plus  $\text{Si}_3\text{N}_4$  or BN plus SiC, is applied on the HPZ fiber surface using a chemical vapor deposition technique or other methods. The compositions, thicknesses, and microstructural morphologies of these surface  
15 coatings on the fibers are selected to provide a weak bonding between the fiber and the matrix which is stable during high temperature composite processing and during use in oxidative environments.

For structural applications requiring low electromagnetic  
20 absorption such as radomes, the surface coating should also display a low dielectric constant. For applications where low absorption is not needed, oxidation-resistant coating compositions other than  $\text{Si}_3\text{N}_4$  over BN could be used, such as SiC over BN. These other applications provide for the use of other  
25 fiber compositions, such as SiC and SiCO. One example is a commercially available small diameter fiber identified as Nicalon.

To demonstrate that the celsian-base glass ceramic matrix composites can be fabricated with desirable mechanical and  
30 physical properties, composites using aligned  $\text{Si}_3\text{N}_4$ /BN- coated HPZ fibers were hot pressed into laminate plates which were then polished and cut into test samples for property evaluation. FIG. 1 shows an optical photograph of a composite panel of BAS glass-

ceramic matrix reinforced with about 20 volume% fibers having a double coating of  $\text{BN/Si}_3\text{N}_4$  and hot pressed at  $1400^\circ\text{C}$  for two hours under 3.5 KSI pressure.

5        FIG. 2 is the scanning electron photomicrograph of a polished cross-section of a double coated fiber-reinforced BAS glass-ceramic matrix composite hot pressed as in FIG. 1 showing uniform fiber distribution and good matrix flow around the fibers. FIGS. 3 and 4 are scanning electron photomicrographs of  
10      the fracture surfaces of the composites showing fiber pull-out indicating the desired tough material behavior. Depending on the intended application, structural and electrical behavior can be controlled and optimized through modifications in interface coatings, fiber architecture, and fiber compositions.

15        Use of small diameter silicon nitride fibers, such as the HPZ fiber, will also allow the fabrication of glass-ceramic composites in complex shaped forms for structural component applications requiring other than plate forms. These fiber-reinforced composites can be fabricated using the same composite  
20      constituent materials described here, but using variations in the processing approach. For example, a technique can be used in which a slurry or sol-gel precursor or polymeric precursor of the ceramic matrix is infiltrated into a woven or other complex shaped preform structure of the small diameter silicon nitride  
25      fibers. In addition, the  $\text{BN/Si}_3\text{N}_4$ ,  $\text{BN/SiC}$ , or other interface coating for the fibers may be applied either prior to formation of the complex fiber preform or after preform formation using infiltration techniques, such as chemical vapor infiltration or sol-gel.

30        The silicon nitride fiber-reinforced BSAS glass-ceramic matrix composites of this invention are new structural materials. The composites fabricated by the methods described above or by some alternate approaches will have low dielectric loss along



with good mechanical strength and fracture toughness compared with existing dielectric materials, particularly at high use temperatures.

5        While several embodiments of the invention have been described it will be appreciated that various structural modifications and procedural step changes may be made without departing from the spirit of the invention or the scope of the subjoined claims.

ABSTRACT OF THE DISCLOSURE

Ceramic Fiber-Reinforced Monoclinic Celsian  
Phase Glass-Ceramic Matrix Composite Material

5           A hydridopolysilazane-derived ceramic fiber reinforced  
monoclinic celsian phase barium aluminum silicate glass-ceramic  
matrix composite material is prepared by ball-milling an aqueous  
slurry of BAS glass powder and fine monoclinic celsian seeds.  
The fibers improve the mechanical strength and fracture toughness  
10 and with the matrix provide superior dielectric properties.

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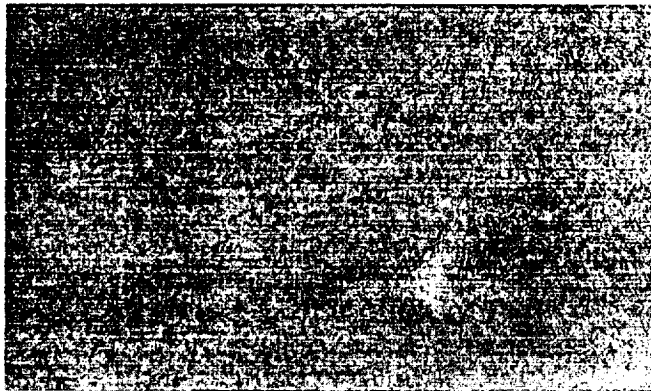


FIG. 1

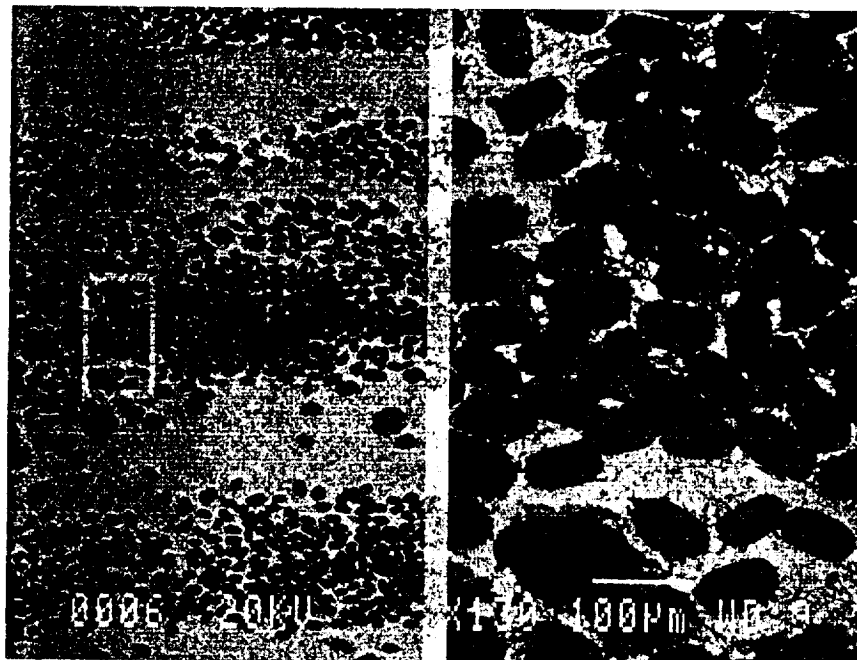


FIG. 2



FIG. 3

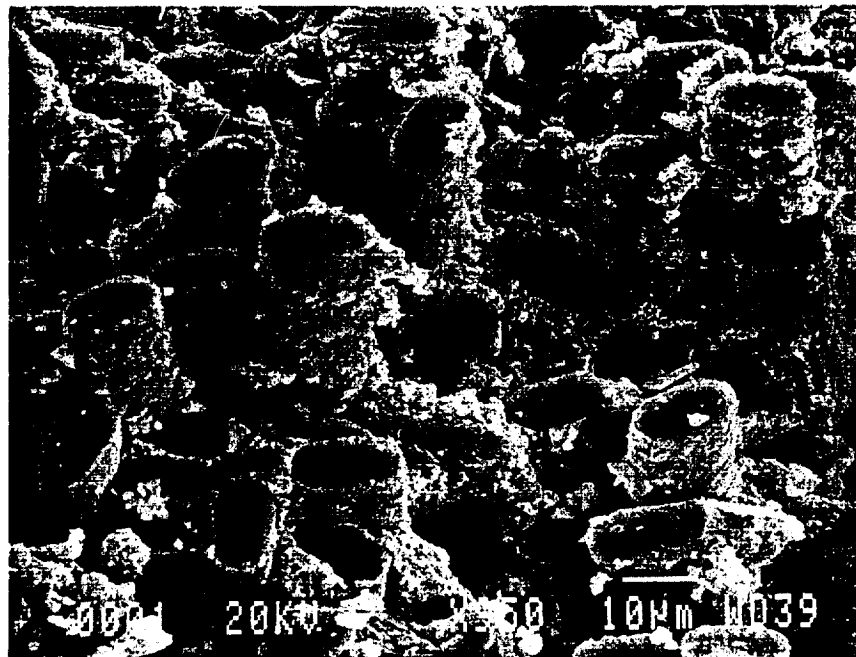


FIG. 4